1,160,945

PATENT SPECIFICATION

NO DRAWINGS

1,160,945

Date of Application and filing Complete Specification: 22 Feb., 1968.
No. 8545/68.
Application made in United States of America (No. 619034) on 27 Feb., 1967.
Complete Specification Published: 6 Aug., 1969.

Index at acceptance: —C7 E3; C5 D(6A4A, 6B1, 6B2, 6B11A, 6B12N1, 6C8)
International Classification: —C 23 g 1/22

COMPLETE SPECIFICATION

Treatment of the Surfaces of Aluminium and its Alloys

We, AMCHEM PRODUCTS, INC., a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Brookside Avenue, Ambler, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to the treatment of, more especially, cleaning and/or etching the surfaces of aluminium and its alloys. After such treatment, the surfaces may be subjected to further processing for example, the formation of a chemical conversion coating or anodic treatment or the like.

It is known to use aqueous alkaline solutions to clean and/or etch the surfaces of aluminium and its alloys. For example, it is known from U.S. Specification Nos. 2,869,267 and 2,939,826 to use for these purposes solutions containing an alkali metal hydroxide and a tertiary amino-alcohol, and it is also known from U.S. Specification Nos. 2,615,846 and 2,584,017 that the addition of an alkali metal gluconate reduces scale formation.

In many cases of cleansing or etching aluminium surfaces, an undesirable precipitate forms in the solutions. The precipitate tends to mar the aluminium surface and interfere with processing treatments later applied to it. Various attempts have been made to overcome this problem by the inclusion of gluconates or tartrates in the solutions, including those containing tertiary amino-alcohols and solvents, and such solutions have been somewhat successful. However it is not yet possible to formulate a single aqueous concentrate of all of the ingredients which can simply be diluted with water for make-up and replenishment purposes. It is therefore necessary in preparing and replenishing aqueous cleaning and/or etching solutions to use separate sources of the active ingredients.

This invention is based upon the discovery that it is possible to make certain stable consolute concentrates of the active ingredients provided that certain conditions are fulfilled.

According to this invention there are provided stable, consolute aqueous concentrates containing, per 1,000 parts by weight,

a) from 46 to 420 parts of an alkali hydroxide;
b) from 1.5 to 300 parts of gluconate ion;
c) from 4.3 to 540 parts of ethyleneglycol or a derivative thereof;
d) from 190 to 640 parts of water; and
e) ethanolamine or a derivative thereof in a proportion of from 17 to 380 parts and sufficient relative to the concentration of ingredients (a), (b) and (c) to yield a stable, consolute aqueous concentrate.

It is necessary that the concentrates be both stable and consolute. By the term "consolute", is meant that the concentrate must be homogeneous to the exclusion of phase separation because a two-phase concentrate is difficult to meter satisfactorily. By the term "stable", is meant that the concentrates must retain their homogeneity when slowly heated in the temperature range of 65°—120°F. A cleaning concentrate which is not so stable will tend to separate into an objectionable two-phase solution during storage and transport.

The content of ethanolamine or derivative thereof should be not less than specified because otherwise an undesirable precipitation of metallic deposits on the aluminium surfaces being treated may occur. Also, the surfaces may not become clean and bright surfaces. The amount can exceed the upper

limit but this is uneconomic. As to the exact concentration of ethanolamine or derivative thereof required to yield the desired stable consolute aqueous concentrates of this invention, there exists a minimum concentration for any given formulation of alkali hydroxide gluconate, ethyleneglycol or derivative thereof. Unless the minimum concentration appropriate to any particular case is used, the necessary stability and consolution will not be obtained. For example, if 25 grams of triethanolamine are added to 10 grams of a representative ethyleneglycol, (the monobutyl ether), 60 grams of potassium hydroxide, 11.5 grams of potassium gluconate and 80.5 grams water, the whole mixed thoroughly and examined, the result is a non-homogenous mixture. Analysis shows the following:

Ingredient	% by Weight
potassium hydroxide	32.0
gluconate ion (as K salt)	6.15
ethyleneglycolmonobutylether	5.34
triethanolamine	13.37
water	43.14

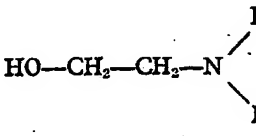
It will be noted that the concentration of each ingredient is within the range specified hereinbefore, yet a stable consolute concentrate is not obtained. This is because the concentration of the triethanolamine is below the minimum necessary for the stability of this particular formulation. If more triethanolamine is dissolved in the mixture, to provide the composition of Example I of the invention below, the result is a stable, consolute, concentrate.

EXAMPLE I
of the invention

	% by Weight
potassium hydroxide	29.85
gluconate ion (as K salt)	5.72
ethyleneglycolmonobutylether	4.98
triethanolamine	19.40
water	40.05

To summarize, the concentration of the ethanolamine compound must be at least about 17 parts and must not exceed 380 parts by weight per 1,000 parts of concentrate. Within this range, the minimum concentration of the ethanolamine or derivative thereof must meet the further requirement of being present in an amount large enough to establish and maintain a consolute stable aqueous concentrate. The minimum concentration of the ethanolamine compound which meets this requirement, is, within the above range, relatively high when the concentrations of other active ingredients (those other than water) is high, and is relatively low within the above range when the concentration of the other active ingredients is low.

Preferably the ethanolamine ingredient is provided by ethanolamine and derivatives thereof, all representable by the general formula



(I)

wherein R^1 is a hydrogen atom or hydroxyethyl (—CH_2 . CH_2 . OH), and R^2 is the same as R^1 or aminoethyl (—CH_2 . CH_2 . NH_2), or an alkyl radical of up to 3 carbon atoms. It is suggested that ethanolamine and derivatives thereof impart a chelating action to the heavy metal ions which enter the solution from alloying components in the aluminium articles, but the invention is not to be limited by this theory. Additional effects of the ethanolamine compound include brightening aluminium surfaces and removing certain soils therefrom.

Where the amount of gluconate ion is less than specified, hard scaly deposits are formed in the solutions. Where the content of gluconate ion exceeds the upper limit a separation of phases in the concentrates may occur.

The gluconate ion may be provided by gluconic acid and/or the sodium and/or potassium salts thereof. If desired, the acid and/or its salts may be dissolved in some water and included in the concentrate as an aqueous solution.

The ethyleneglycol ingredient must be present in the specified proportions since where less is used, cleaning of metal surfaces is not satisfactory while when more is used, the stability of the concentrate tends to be upset. It is essential to provide an adequate level of soil removal from the articles being treated. Preferably this ingredient is provided by the compounds of the formula:

$$R^3—O—CH_2—CH_2—O—R^4 \qquad \text{(II)}$$

wherein R^3 is a hydrogen atom or an alkyl group of up to 4 carbon atoms, and R^4 is the same as R^3 or the group —R^5H or —R^5—CH_2—CH_2OH where R^5 is the linkage —$(CH_2)_2O$—. Such derivatives are advantageous because of their water-solubility and tolerance of inorganic ions.

The water must be present in an amount of from 19% to 64% by weight, based on the total weight of the concentrate. Where less is used, the improved stability is not always obtained, while when more than the specified amount of water is used, the solutions made up do not provide commercially-feasible cleaning and/or etching solutions.

Although the gluconate ion and/or alkaline hydroxide may be added in the form of their sodium salts, it is recommended that for

maximum physical stability, the sodium ion be employed only in relatively small amounts, especially in concentrates containing large amounts of the ethyleneglycol ingredient and/or small amount of water. The potassium ion is preferred.

The concentrate of this invention may be prepared by mixing ingredients (a), (b) and (c) in ingredient (d) to form a two-phase system. Then sufficient of ingredient (e) is added to convert the two-phase system into the desired stable consolute concentration of this invention. Adding ingredient (e) last ensures that one can easily determine the minimum concentration of this ingredient within its indicated range necessary to form the stable consolute concentrate for the particular formulation.

The cleaning concentrates are used in diluted form for cleaning and/or etching aluminium. Generally, they are diluted with water for use, sufficient water being employed to yield a final concentration, for example, of from 1 gram to 15 grams per litre of alkali hydroxide, and the surfaces of aluminium and its alloys may be cleaned and/or etched therein by contact therewith for an appropriate time at an appropriate temperature.

This invention extends to the concentrates, methods of making them and methods of making from them solutions to clean and etch the surfaces of aluminium and its alloys and also to the surfaces when so cleaned and/or etched.

In order that this invention may be well understood, further Examples will now be given, though by way of illustration only, of preferred stable consolute concentrates. All parts are expressed as % by weight and the temperature range (where indicated) is that over which the concentrate remains stable and consolute.

EXAMPLE II

potassium hydroxide	31.48
gluconate ion (as K salt)	6.98
ethyleneglycolmonobutylether	5.62
triethanolamine	17.46
water	38.46

EXAMPLE III

potassium hydroxide	19.40
gluconate ion (as K salt)	0.97
ethyleneglycolmonobutylether	1.94
triethanolamine	28.22
water	49.47

up to 190°F.

EXAMPLE IV

potassium hydroxide	14.70
gluconate ion (as K salt)	2.93
ethyleneglycolmonobutylether	14.70
triethanolamine	27.93
water	39.64

up to 190°F.

EXAMPLE V

potassium hydroxide	29.98
gluconate ion (as K salt)	4.98
ethyleneglycolmonobutylether	5.72
triethanolamine	19.40
water	40.00

22°F—>190°F.

EXAMPLE VI

potassium hydroxide	35.96
gluconate ion (as K salt)	5.96
diethyleneglycolmonoethylether	3.34
N-methyl-diethanolamine	6.82
water	48.02

<0°F.—144°F.

EXAMPLE VII

potassium hydroxide	23.20
gluconate ion (as K salt)	6.70
diethyleneglycolmonoethylether	15.82
triethanolamine	11.53
water	42.75

<0°F.—162°F.

EXAMPLE VIII

potassium hydroxide	11.50
gluconate ion (as K salt)	1.92
sodium hydroxide	2.09
ethyleneglycol	13.22
ethanolamine	14.17
water	57.10

<0°F.—>190°F.

EXAMPLE IX

potassium hydroxide	41.98
gluconate ion (as K salt)	4.57
ethyleneglycolmonomethylether	2.43
diethanolamine	1.74
water	49.28

<0°F.—>190°F.

EXAMPLE X

potassium hydroxide	18.55
gluconate ion (as Na salt)	3.71
triethylene glycol	9.09
ethyleneglycolmonoethylether	3.80
N-methyl-diethanolamine	6.40
water	58.45

<0°F.—>190°F.

EXAMPLE XI

potassium hydroxide	32.10
gluconate ion (as K salt)	5.63
ethyleneglycolmonobutylether	5.96
triethanolamine	18.15
surfactant (Triton* DF-12, an ethoxylated straight chain alcohol)	0.43
water	37.73

(*Note: TRITON is a Registered Trade Mark)

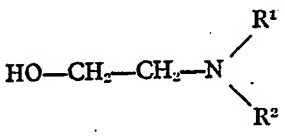
In each case, the concentrate was prepared by dissolving the potassium hydroxide, gluconate ion and ethylene-glycol ingredient in the water and then adding the ethanolamine ingredient until a stable, consolute concentrate was obtained.

WHAT WE CLAIM IS:—

1. A stable consolute aqueous concentrate containing per 1,000 parts by weight

a) from 46 to 420 parts of an alkali hydroxide;
b) from 1.5 to 300 parts of gluconate ion;
c) from 4.3 to 540 parts of ethyleneglycol or a derivative thereof;
d) from 190 to 640 parts of water;
e) ethanolamine or a derivative thereof in a proportion of from 17 to 380 parts and sufficient relative to the concentration of ingredients (a), (b) and (c) to yield a stable, consolute, aqueous concentrate.

2. A concentrate as claimed in Claim 1, in which ingredient (e) is provided by a compound of the general formula:



where R^1 is a hydrogen atom or hydroxyethyl and R^2 is the same as R^1 or aminoethyl or an alkyl radical of up to 3 carbon atoms.

3. A concentrate as claimed in Claim 1 or Claim 2, in which ingredient (e) is provided by triethanolamine.

4. A concentrate as claimed in any of the preceding Claims, in which ingredient (a) is provided by potassium or sodium hydroxide.

5. A concentrate as claimed in any of the preceding Claims, in which ingredient (b) is provided by gluconic acid and/or the sodium and/or potassium salts thereof.

6. A concentrate as claimed in any of the preceding Claims, in which ingredient (c) is provided by a compound of the general formula:

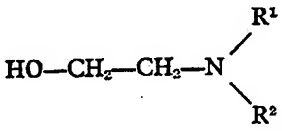
$$R^3—O—CH_2—CH_2—O—R^4$$

where R^3 is a hydrogen atom or an alkyl group of up to 4 carbon atoms, and R^4 is the same as R^3 or is the group $—R^5H$ or $—R^5—CH_2—CH_2—OH$ where R^5 is the linkage $—(CH_2)_2O—$.

7. A concentrate as claimed in Claim 6, in which ingredient (c) is provided by ethyleneglycolmonobutylether.

8. A stable consolute aqueous concentrate as claimed in any of the preceding Claims, containing per 1,000 parts,

a) from 46 to 420 parts of sodium and/or potassium hydroxide;
b) from 1.5 to 300 parts of gluconate ion;
c) from 4.3 to 540 parts of a compound of the general formula:



(wherein R^1 is a hydrogen atom or hydroxyethyl, and R^2 is the same as R^1 or aminoethyl or an alkyl group of up to 3 carbon atoms);

d) from 190 to 640 parts of water; and
e) a compound of the general formula:

$$R^3—O—CH_2—CH_2—O—R^4$$

(where R^3 is a hydrogen atom or an alkyl group of up to 4 carbon atoms, and R^4 is the same as R^3 or the group $—R^5.H$ or the group $—R^5.CH_2.CH_2.OH$ where R^5 in the linkage $—(CH_2)_2.O—$), in a proportion of 17 to 380 parts and sufficient relative to the concentration of ingredients (a), (b) and (c) to yield a stable consolute aqueous concentrate.

9. A concentrate as claimed in any of the preceding Claims, substantially as described herein.

10. A stable, consolute, aqueous concentrate substantially as described herein with reference to any of the Examples.

11. A method of making a stable, consolute, aqueous concentrate as claimed in any of the preceding Claims, comprising mixing ingredients (a), (b) and (c) in (d), and adding sufficient of ingredient (e) to form the desired concentrate.

12. A stable, consolute, aqueous concentrate whenever made by the method of Claims 11.

13. A method of making an aqueous solution for the treatment of the surface of aluminium or an alloy thereof comprising diluting a concentrate as claimed in any of Claims 1 to 10 and 12 with water until the concentration of ingredient (a) is from 1 to 15 grams per litre.

14. An aqueous solution of the treatment of the surface of aluminium or an alloy thereof whenever made by the method of Claim 13.

15. A method of cleaning and/or etching a surface of aluminium or an alloy thereof comprising contacting it with an aqueous

solution as claimed in Claim 14 for such a time and at such a temperature to clean and/or etch.

16. A surface of aluminium or an alloy thereof whenever cleaned and/or etched by the method of Claims 15.

For the Applicants,
SANDERSON & CO.,
Chartered Patent Agents,
97 High Street,
Colchester,
Essex.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2. from which copies may be obtained.